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ORIGINAL PAPER

Stilbene-Like Molecules as Fluorescent Probes Applied for Monitoring of Polymerization Process

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Abstract 2-(*p-N*,*N*-dimethylaminostyryl)benzoxazole(**OS**), 2-(*p-N*,*N*-dimethylaminostyryl)-benzothiazole (**SS**) and 2-(*p-N*,*N*-dimethylaminostyryl)naphtiazole (**PS**) were prepared and their absorption and fluorescence spectra were measured in various solvents at room temperature. On the basis of the solvatochromic behavior the ground state (μ_g) and excited state (μ_e) dipole moments of these *p-N*,*N*-dimethylaminostyryl derivatives were evaluated. The dipole moments (μ_g and μ_e) were estimated from solvatochromic shifts of absorption and fluorescence spectra as function of the dielectric constant (ε) and refractive index (n) of applied solvents. The absorption spectra only slightly are affected by the solvent polarity in contrast to the fluorescence spectra that are highly solvatochromic and display a large Stokes shift. The analysis of the solvatochromic behavior of the fluorescence spectra as function of Δf (ε, n) revealed that the emission occurs from a high polarity excited state. The large dipole moment change along with the strongly red-shifted fluorescence, as the solvent polarity is increased, demonstrate the formation of an intramolecular charge transfer state (ICT). Compounds under the study were used as fluorescence probes for monitoring the kinetics of polymerization. The study on the changes in fluorescence intensity and spectroscopic shifts of studied compounds were carried out during thermally initiated polymerization of methyl methacrylate (MMA) and during photoinitiated polymerization of 2-ethyl-2-(hydroxymethyl)propane-1,3-diol triacrylate (TMPTA).

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Introduction

The photophysical properties of different benzoxazole and benzothiazole derivatives have been studied intensively for several decades due to their potential applications in molecular electronics and biological fluorescence probing [1]. Therefore, the synthesis of highly fluorescent compounds has gained considerable interest. For the applications as fluorescence probe, the detailed information about their spectroscopic properties is needed. It is well known that different 2-aryl-substituted benzoxazole derivatives are highly fluorescent [2] exhibiting a dual fluorescence with large Stokes shift. Compounds of this type have been widely used as effective light protectors as well as lasing materials for lasers [1, 3].

Such compounds are also applied as the fluorescence probes, used in chemistry for monitoring specific properties of the medium in which they are incorporated [4, 5]. It is possible because their fluorescence is sensitive to changes in temperature, polarity or rigidity of the environment. Therefore, one can use them to estimate polarity of medium or degree of cure by measuring the changes in their emission intensity or value of the emission maximum shift.

Fluorescence probes may be the aromatic compounds possessing electron donor-acceptor chromophores and exhibiting dual fluorescence. They are of particular interest because their fluorescence is usually associated with the formation of a highly polar electronic state. Such a polar state is due to an electron transfer process and is referred as an intramolecular charge transfer (ICT) state. Charge transfer states have large

dipole moments, so the energies of the excited state are expected to be highly sensitive to the solvent polarity [1]. That is why, the compounds exhibiting the presence of ICT state can be used as spectroscopic probes.

An important application of fluorescence probes in polymer chemistry is a monitoring of the polymerization process.

The classical fluorescence probes possessing typical ICT (e.g. series of *p*-(*N, N*-dialkylamino)benzylidene malononitryles) were described by Loutfy [6–8]. Very spectacular are properties of ICT probe described by Verhoeven's research group, who tested the properties of 1-phenyl-4-(4-cyano-1-naphtylmethylene)piperidine ("Fluoroprobe") [9–11]. It was found that this molecule emits charge-transfer-type fluorescence with the quantum yield exceeding 0.5 and displays the enormous solvatochromism of this fluorescence making this molecule attractive as fluorescent polarity and viscosity probe. The well known ICT probes applied for monitoring of polymerization kinetics are also 4-(*N,N*-dimethylamino)-4′-nitrostilbene [12], 2-*N,N*-dimetylamino-7-nitrofluorone [13], dansylamide [14], carbazole derivatives and 9,9′-dianthryl [15], stilbene and coumarin derivatives [12].

Fayed *et al*. documented that the spectroscopic properties of selected styrylbenzoxazoles are sensitive to the properties of a bulk solvent [16, 17]. It is our intention to extend this study on new, highly polar styrylbenzoxazole applied as fluorescence probes monitoring a progress of free radical polymerization.

In this paper, we report the synthesis of three solvatochromic fluorescent probes (see Chart 1). The influence of solvents of various polarity on their electronic absorption and fluorescence spectra are reported as well. The evaluation of their dipole moments in the excited state using solvatochromic method is also presented.

We describe the relationship between the change in the emission spectra of the three structurally different compounds and degree of monomer conversion during thermally initiated polymerization of monomethacrylate and photopolymerization of polyolacrylate.

Experimental section

Materials

Methyl methacrylate (MMA), 2-ethyl-2-(hydroxymethyl) propane-1,3-diol triacrylate (TMPTA) and all spectroscopic grade solvents used for spectroscopic measurements were purchased from Aldrich. All chemicals and solvents were of the best grade quality and were used without further purification. Methyl methacrylate, before use, was purified using conventional methodology.

Spectral measurements

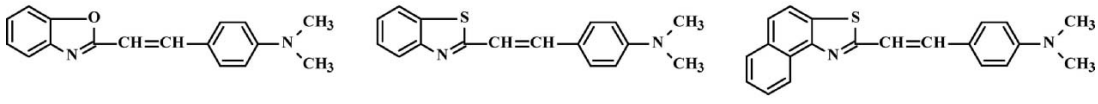
For the measurements of the absorption and emission spectra and fluorescence quantum yield (Φ) the 1.0×10^{-5} M solutions of tested compounds in various solvents were prepared. At such concentration no aggregation or self-absorption effects of the dyes were observed [18]. Absorption spectra were recorded at room temperature using a Varian Cary 3E spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter. Absorption and emission spectra were recorded with a spectroscopic quality: hexane, cyclohexane, methyl methacrylate (MMA), ethyl acetate (AcOEt), tetrahydrofuran (THF), dichloromethane, butyronitrile (BuCN), methanol (MeOH), *N,N*-dimethylformamide (DMF) and water. The fluorescence measurements were performed at an ambient temperature.

The fluorescence quantum yields measurement: The fluorescence spectrum of a dilute (<25 μM) dye solution was recorded by the excitation at the absorption band maximum of the reference. A dilute Coumarin I in ethanol was used as reference. The fluorescence spectrum of Coumarin I was obtained by excitation at its absorption peak at 418 nm. The quantum yield of the dye (Φ_{dye}) was calculated using equation:

$$\Phi_{dye} = \Phi_{ref} \frac{I_{dye} A_{ref}}{I_{ref} A_{dye}} \quad (1)$$

where Φ_{ref} is the fluorescence quantum yield of reference sample (Coumarin I) in ethanol ($\Phi = 0.64$) [19], A_{dye} and A_{ref} are the absorbances of the dye and reference samples at

Chart 1



OS **SS** **PS**

their excitation wavelengths, I_{dye} and I_{ref} are the areas arbitrary units of the corrected fluorescence spectra (plotted in frequency scale) for the compounds and reference samples, respectively.

The ^{1}H NMR spectra were recorded with the use of a Varian spectrometer Gemini 200 operating at 200 MHz. Dimethylsulfoxide (DMSO) was used as the solvent and tetramethylsilane (TMS) as internal standard.

Melting points (uncorrected) were determined using Boëthius apparatus.

Monitoring the free radical polymerization of monoacrylate

Deoxygenated methyl methacrylate solution, containing benzoyl peroxide as thermal free radical polymerization initiator (1%), and tested probe, at concentration giving the intensity at the absorption maximum in the range of about 0.3, was placed in pyrex test tubes. Polymerization was initiated at 55°C. The samples were periodically (15 or 20 min) removed from the water bath and cooled with ice to temperature of about 0°C in order to stop the polymerization and than warm-up to room temperature. The fluorescence of solutions was measured after subsequent time of polymerization and degrees of polymerization were estimated by gravimetrical method after precipitation of polymer in ethanol.

Monitoring the free radical polymerization of polyolacrylate

Studies on the changes of probes fluorescence during polymerization initiated photochemically were carried out using 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and IRGACUR 184 as initiator (2%), concentration of the tested fluorescence probe was about 0.25%. A thin film of this mixture was prepared between two sheets of polyethylene foil, separated by a ring of aluminium foil to prevent the outflow of the mixture. The film was irradiated using UV emission of xenon lamp type XBO 150W (OSRAM). The emission spectra and double bond conversion (measured by following the disappearance of C=C stretch at 810 cm^{-1} using FTIR spectroscopy (Fourier transformation—infra-red absorption spectroscopy)) were measured after subsequent irradiations.

Theoretical calculations

Onsager cavity radii (a) for all molecules tested were determined theoretically using the molecules optimized geometry. *Ab initio* calculations were carried out using B3 LYP/6-31 G (2df,2p) method to estimate the ground state dipole moments of the dye molecules under investigation. All calculations were carried out with Gaussian 03 program [20].

Synthesis

All tested fluorophores were prepared according to general method presented in Scheme 1 for 2-methylbenzoxazole and 2-methylbenzothiazole, respectively for illustration.

The dyes were obtained starting from the *p*-(*N*,*N*-dimethylamino)benzaldehyde and 2-methylbenzoxazole, 2-methylbenzothiazole and 2-methyl-α-napthothiazole yielding *p*-(*N*,*N*-dimethylaminostyryl)benzoxazole (**OS**), *p*-(*N*,*N*-dimethylaminostyryl)benzothiazole (**SS**) and *p*-(*N*,*N*-dimethylaminostyryl)-α-napthothiazole (**PS**), respectively.

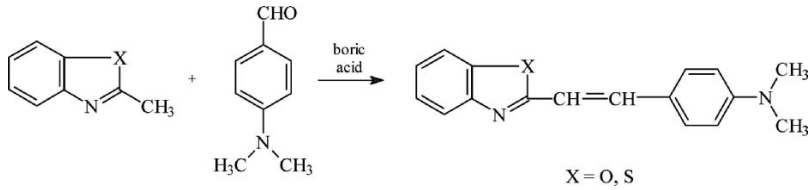
*2-(p-N,N-Dimethylaminostyryl)benzoxazole (**OS**)*

A mixture of equimolar amounts of *p*-(*N*,*N*-dimethylamino) benzaldehyde and 2-methylbenzoxazole was heated at 195–200°C for 5 h in presence of boric acid (0.05 g per 0.01 M of aldehyde) [21]. The obtained powder was recrystallized from ethanol, filtered and dried at ambient temperature. The reaction yield was 62%; m.p. 170–173°C,^{1}H NMR DMSO-d6: δ 2.982 (s, 6H, –CH_3), 6.715–6.760 (d, 2H, Ar), 6.922–7.003 (d, $J = 16.2$ Hz, 1H, –CH=), 7.306–7.352 (m, 2H, Ar), 7.585–7.630 (d, 2H, Ar), 7.650–7.667 (m, 2H, Ar), 7.732 (s, 1H)

*2-(p-N,N-Dimethylaminostyryl)benzthiazole (**SS**)*

2-Methylbenzothiazole (14.9 g, 1 mol), *p*-(*N*,*N*-dimethylamino)benzaldehyde (14.9 g, 1 mol) and concentrated hydrochloric acid (3 ml) were heated at 100°C for 16 h. After being made alkaline (crude yield 96%) the product was recrystallized from methyl alcohol [22]. The reaction yield was 78%; m.p. 205–208°C,^{1}H NMR DMSO-d6: δ 2.976 (s, 6H, –CH_3), 6.714–6.759 (d, 2H, Ar), 7.244–7.324 (d, $J = 16$ Hz, 1H, –CH=), 7.357–7.429 (m, 1H, Ar), 7.458–7.749 (m, 1H, Ar), 7.498–7.505 (d, $J = 14$ Hz, 1H, –CH=), 7.559–7.604 (d,

Scheme 1 The general route for synthesis of the tested compounds



2H, Ar), 7.859–7.869 and 7.901–7.908 (m, 1H, Ar), 7.996–8.003 and 8.035–8.046 (m, 1H, Ar)

*2-(p-N,N-dimethylaminostyryl)-α-napthothiazole (**PS**)*

The compound was prepared by heating of 2-methyl-α-napthothiazole (0.5 g), *p*-(*N*,*N*-dimethylamino)benzaldehyde (0.4 g) and zinc chloride (0.5 g) at 160–180°C for 90 min. The crude product was recrystallized from light petroleum to yield yellow powder [23].

^{1}H NMR DMSO-d6: δ 2.983 (s, 6H, –CH_3), 6.728–6.773 (d, 2H, Ar), 7.316–7.396 (d, $J = 16.8$ Hz, 1H, –CH=), 7.558–7.670 (m, 5H, Ar), 7.976–8.096 (m, 1H (–CH=) and 3H Ar).

Results and discussion

Solvatochromism of the stilbene-like molecules

The data characterizing the absorption and emission properties of the styryl dyes tested (**OS**, **SS**, **PS**) are summarized in Table 1 .

The normalized absorption and emission spectra of **PS** in three different solvents are shown in Fig. 1 for illustration.

All the electronic absorption spectra display two main bands whose maxima are located in the 280–300 and 400 nm regions. The short wavelength bands are attributed to the $\pi \rightarrow \pi *$ transitions whereas the long-wavelength bands, generally characterized by higher molar absorption coefficient, are attributed to CT transitions. On varying the solvent polarity, relatively small shifts in the absorption maxima are observed (15–17 nm).

From the inspection of the data from Table 1 it is seen that probes **OS** and **SS** show unusual absorption band behavior in water (absorption band maxima about 350 nm). This is probably due to the probes aggregation in water [16,

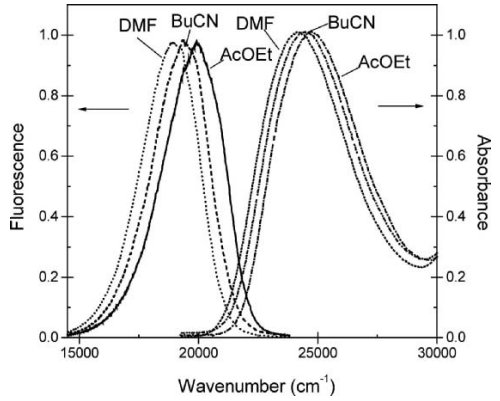


Fig. 1 Normalized absorption and fluorescence spectra of **PS** in: ethyl acetate (AcOEt), butyronitrile (BuCN) and *N*,*N*-dimethylformamide (DMF) as solvents

Table 1 Absorption (λ_{abs}) and emission (λ_{em}) maxima and fluorescence quantum yields of the probes under the study in various solvents

Solvent	*n*	ε	**OS**			**SS**			**PS**		
			λ_{abs} (nm)	λ_{em} (nm)	φ_{fl}	λ_{abs} (nm)	λ_{em} (nm)	φ_{fl}	λ_{abs} (nm)	λ_{em} (nm)	φ_{fl}
Hexane	1.3748	1.8863	376	431		383	447		397	480	
Cyclohexane	1.4262	2.023	378	438	0.015	385	453	0.007			0.09
Methyl methacrylate	1.414	2.90	386	469		393	493				
Ethyl acetate	1.3724	6.053	385	471		397	491		404	502	
THF	1.4071	7.58	389	477	0.035	398	490	0.016	408	502	0.02
Dichloromethane	1.4242	8.93	391	477	0.015	400	496	0.006	440	503	0.09
Butyronitrile	1.384	20.3	389	478	0.015	395	499	0.007	409	517	0.01
Methanol	1.3284	32.66	390	500	0.008	400	510	0.001	406	530	0.005
DMF	1.4304	36.71	393	489	0.014	401	511		412	529	
Water	1.3329	80.16	352	539	0.015	350	505	0.008			0.011

17]. The fluorescence emission spectra of the probes show only one peak in solvents used. The fluorescence maxima of tested compounds are significantly red-shifted in comparison to the their absorption spectra. The shift enhances as solvent polarity increases. The fluorescence quantum yield of 2-(*p*-*N*,*N*-dimethylaminostyryl)benzoxazole (**OS**), 2-(*p*-*N*,*N*-dimethylaminostyryl)benzothiazole (**SS**) and 2-(*p*-*N*,*N*-dimethylaminostyryl)-α-napthothiazole (**PS**) in THF is rather small and amounts 0.035, 0.016 and 0.02, respectively.

The correlations between the absorption and emission maxima wavelengths and the Dimroth–Reichardt empirical solvent polarity parameter $E_T(30)$ [24] are shown in Figs. 2 and 3. As can be seen, both the absorption and the emission maxima correlate well with solvent polarity parameters. The slopes of the lines are indicative of the sensitiveness of the different probes towards solvent polarity.

In Fig. 2, the absorption maxima of all tested compounds present the same sensitivity towards polarity, as indicated by similar slopes of all plots. It means that the size of the probe does not affect very much the solute-solvent interactions when benzoxazole and benzothiazole rings are changed on napthothiazole ring.

It is important to note that the tested compounds are sensitive to solvent polarity in both the ground and excited singlet states [16, 17].

Dipole moment determination

The universal interaction between solute and solvent molecules is due to a solvent acting as a dielectric medium. Therefore, according to Bakshiev [25], Chamma and Viallet [26] the shift between the absorption and emission spectra is related to the dielectric constant and the refractive index of solvent [27].

Based on quantum mechanical perturbation theory and Inamdar's studies on the absorption (ν_{ab}) and fluorescence

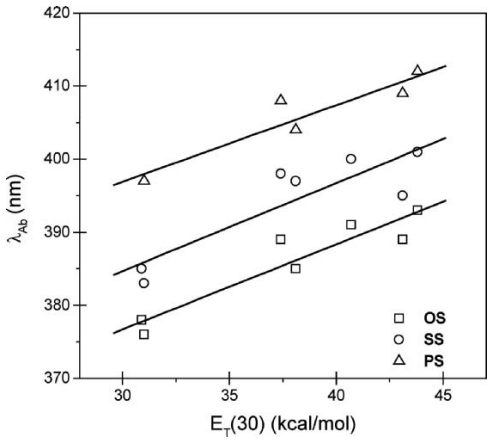


Fig. 2 Correlation between the absorption maxima of the probes and $E_T(30)$ empirical polarity parameter [24]

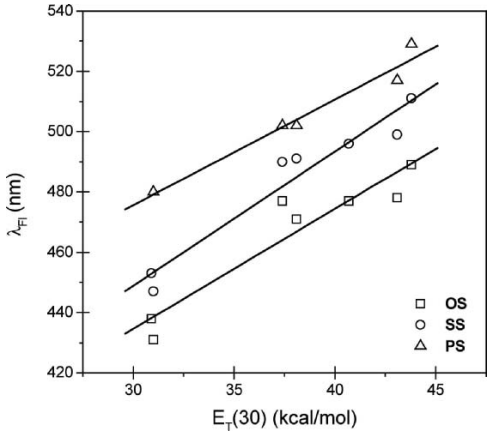


Fig. 3 Relationship between the emission maxima of the probes and $E_T(30)$ empirical polarity parameter [24]

(ν_{fl}) band shift of a spherical solute in solvents of varying permittivity (ε) and refractive index (n), the changes of the spectroscopic properties of the solute can be characterized by the difference in the absorption and fluorescence maxima positions.

$$\nu_{ab} - \nu_{fl} = m_1 f(\varepsilon, n) + \text{const.} \tag{2}$$

The model of dipole in a dielectric medium that is used to derive Eq. (2) also gives Eq. (3) for the sum of $\nu_{ab} + \nu_{fl}$.

$$\nu_{ab} + \nu_{fl} = m_2 [f(\varepsilon, n) + 2g(n)] + \text{const.} \tag{3}$$

ν_{ab} and ν_{fl} are the peak of absorption and emission (steady-state fluorescence) frequencies, where

$$f(\varepsilon, n) = \frac{(2n^2+1)}{(n^2+2)}\left[\frac{(\varepsilon-1)}{(\varepsilon+2)} - \frac{(n^2-1)}{(n^2+2)}\right] \tag{4}$$

is solvent polarity parameter [11] and

$$g(n) = \frac{3}{2}\left[\frac{(n^4-1)}{(n^2+2)^2}\right] \tag{5}$$

with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{6}$$

and

$$m_2 = \frac{2\left(\mu_e^2 - \mu_g^2\right)}{hca^3} \tag{7}$$

where h is Planck's constant, c is the velocity of light in vacuum, μ_g and μ_e are the dipole moments in the ground and excited states, respectively. The parameters m_1 and m_2

can be obtained from the absorption and fluorescence band shifts (Eqs. (2) and (3)). The Onsager radius a of the solute molecule can be determined by *Ab initio* calculations.

The difference in energy between the absorbed and emitted radiation is known as the Stokes shift. One of the primary cause of Stokes shift is solvent relaxation. The Lippert equation is a simple and the most widely used expression to explain the general solvent effects (due to the dielectric constant (ε) and the refractive index (n) of the solvent). The specific solvent effects can be easily recognized as deviation from the predictions of the Lippert equation. The Lippert expression can be represented as follows:

$$\text{Stokes shift} = \frac{2(\mu_e - \mu_g)^2}{hca^3}\left[\frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)}\right] + \text{constant} \quad (8)$$

The term in brackets in Eq. (8) with the dielectric constant (ε) and the refractive index (n) of the solvent is called the orientational polarizability (Δf)

$$\Delta f = \left(\frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)}\right) \quad (9)$$

and is linearly related to the Stokes shift [18].

It should be noted that, the solvent polarity function $f(\varepsilon, n)$ used for calculations is different from Lippert–Mataga function [28].

The spectral shift obtained basing on the absorption and emission spectra are correlated with the polarity parameters (dielectric constant and refractive index) of solvents. Figures 4 and 5 present the spectral shifts (in cm^{-1}) $\nu_{ab} - \nu_{fl}$ and $\nu_{ab} + \nu_{fl}$ for **OS**, **SS** and **PS** versus the solvent polarity function $f(\varepsilon, n)$ and $f(\varepsilon, n) + 2g(n)$, respectively. As can be seen from Figs. 4 and 5 the data fit to the straight lines.

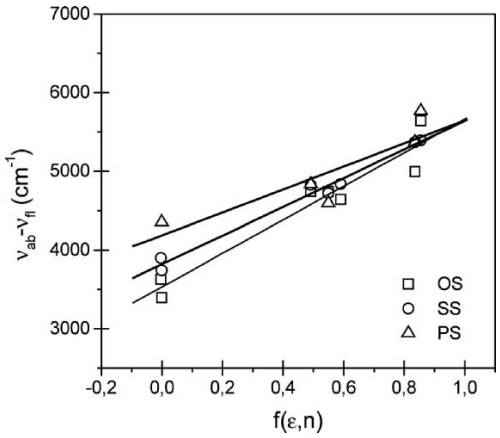


Fig. 4 Plot $\nu_{ab} - \nu_{fl}$ (cm^{-1}) versus $f(\varepsilon, n)$ for **OS**, **SS** and **PS** in different solvents

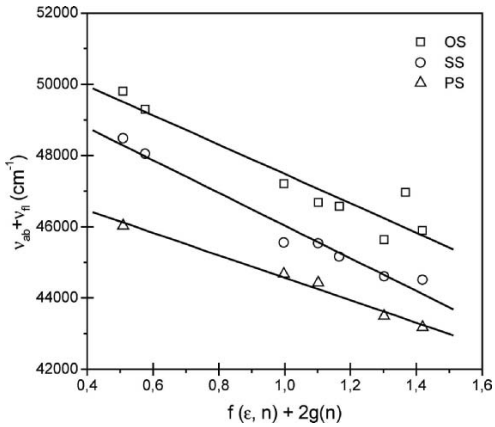


Fig. 5 Plot of $\nu_{ab} + \nu_{fl}$ (cm^{-1}) versus $f(\varepsilon, n) + 2g(n)$ for **OS**, **SS** and **PS** in different solvents

The dipole moments estimated from the obtained linear relationships for all dyes tested are summarized in Table 2.

As it was mentioned earlier, the values of μ_e and μ_g were determined using spectral shift (Eqs. (6) and (7)) whereas μ_g were determined theoretically. The estimated dipole moments of the excited state of styryl bases range from 11.8 to 17 Debye. The difference in the excited and ground state dipole moments $\Delta\mu = \mu_e - \mu_g$ oscillate in the range from 7 to 12 D. Such change in dipole moment corresponds to an intramolecular displacement of a charge upon excitation in the range from 1.4 to 2.42Å.

Inspection of the data in Table 2 reveals that for all molecules under investigation, the changes in the dipole moments on the electronic excitation are significant. This suggests that the emission of these compounds originate from states, which are more polar than ground state [18].

Monitoring the degree of free radical polymerization of mono and polyolacrylates

The first objective of this study was to investigate the fluorophores response to viscosity changes that occur during thermally initiated polymerization of methyl methacrylate (MMA). All the probes were well soluble both in the monomers and in the solid polymers. There was no indication that during the course of polymerization molecular aggregates are formed or precipitation of the probes occurs.

Figure 6 shows the fluorescence spectra of **OS** probe during MM thermally initiated polymerization recorded for different degrees of polymerization. The changes of the fluorescence intensity, observed at the fluorescence maximum, show its gradual increase when a liquid solution transfers into solid polymer matrix.

Fluorescence intensity increases due to changes in viscosity of the probe microenvironment that occurs during the polymerization. This behavior is attributed to the intramolecular charge transfer excited state relaxation to a lower energy

Table 2 Geometrical parameters, slope of Bakshiev's correlation and calculated excited state dipolar moments for tested probes

Compound	Slope (cm^{-1})[a]	Slope (cm^{-1})[b]	Volume (Å^3)	μ_g (D)	μ_e (D)
OS	2133.49	4119.49	153	5.40	17.0
SS	1822.86	4574.64	146	5.08	11.8
PS	1459.44	3153.15	202	5.05	16.0

[a]From Fig. 4.

[b]From Fig. 5.

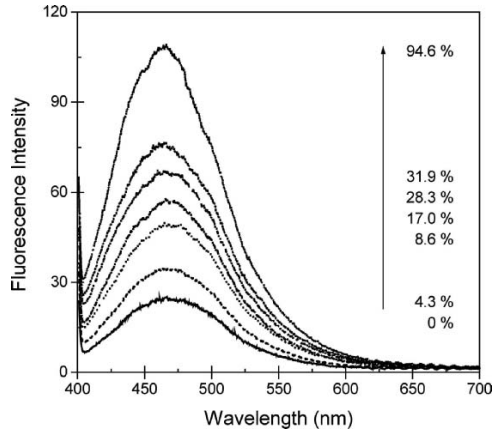


Fig. 6 Changes in the fluorescence spectra of **OS** during thermally initiated polymerization of methyl methacrylate recorded for different degree of monomer conversion into a rigid polymer matrix

charge transfer states obtained by rotation about the single and double bonds of the molecule [29]. In general, in such case, the radiative deactivation constant is not affected, but a decrease in the non-radiative deactivation constant is related to an increase in the environment viscosity [30].

Figure 7 summarizes the changes in fluorescence intensity observed for the **SS** probe during thermally initiated polymerization of MMA.

A characteristic behavior is observed in Fig. 7. The fluorescence intensities, measured at a wavelength specific for each probe, changes insignificantly until a critical point of polymerization is reached where a sharp increase in the fluorescence intensity occurs. The "S" shape of curve on polymerization time is a common behavior and is observed in the polymerization that shows the distinct transition from fluid to a rigid glass [6–8]. The specific behavior of the probes in the transition area of fluid monomer to a rigid polymer is explained by the increase in viscosity and this, in turn, rapidly decreases the efficiency of nonradiative deactivation of the emitting state. As a result one observes an increase in fluorescence intensity. In other words, as monomer consumption increases due to the polymerization, probe molecules are starting to be trapped in the rigid poly(methyl methacrylate) (PMMA) environment. Below the time needed for the onset of the gel effect, since the probe molecules are relatively free, they can easily relax to the ground state. This causes a low fluorescence intensity of the probe. However, above the time needed for the onset of the gel effect, since the reaction mixture is highly viscous and the relaxation processes become less effective, emission intensity can rise to higher value. In general, the specific behavior of the probes in the transition area of fluid monomer to a rigid polymer is explained by the increase in viscosity and this, in turn, decreases the efficiency of nonradiative deactivation of the emitting state.

An increase in intensity of probe fluorescence was also observed during the photochemically initiated polymerization of TMPTA with gradual increase of degree of monomer double bond conversion. Figure 8 shows illustrative

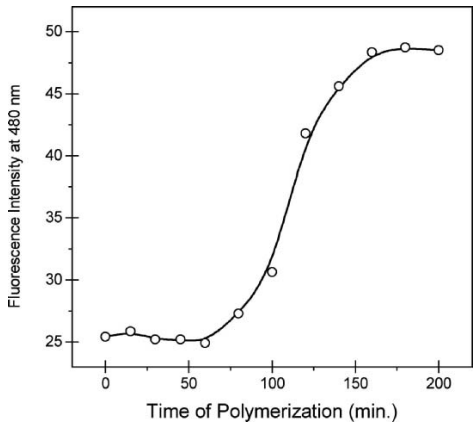


Fig. 7 Changes in fluorescence intensity (measured at $\lambda = 480$ nm) for **SS** probe during thermally initiated polymerization of methyl methacrylate in the presence of benzoyl peroxide (1%)

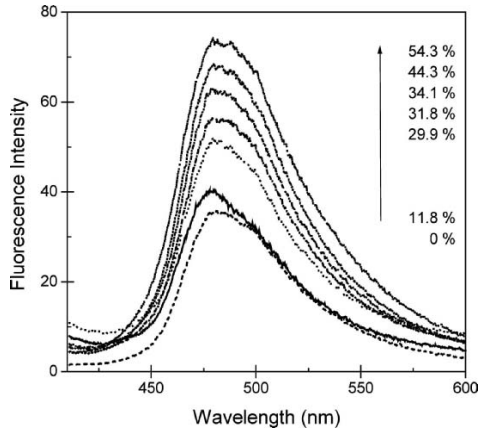


Fig. 8 Emission spectra of **OS** for different degrees of photoinitiated polymerization of TMPTA. The degree of polymerization was measured using FTIR spectroscopy

emission spectra of **OS** probe for different degrees of TMPTA polymerization.

As can be seen, fluorescence of the probe changes gradually with progressive disappearance of the monomer double bond for all measurement range. No sudden increase caused by the rigid gel origination is observed. The increase in probe's emission intensity *versus* monomer double bond conversion is well-defined linear function in all cases with high correlation coefficient.

Figure 9 shows this type of relationships plotted for 2-(*p-N*,*N*-dimethylaminostyryl)benzoxazole (**OS**) as the probe.

The slope of the linear relationship shown in Fig. 9 can be a measure of the probes "sensitivity." The measurements performed for all probes showed that the probe **PS** is the lowest sensitivity. The most sensitive probe is 2-(*p-N*,*N*-dimethylaminostyryl)benzoxazole (**OS**).

It is necessary to emphasize that in literature one can find reports showing that, probes very often react with the free radicals formed from an initiator or in the case of the photoinitiation *via* electron transfer reaction, photooxidize or photoreduce [4, 31]. This causes very often the decrease or even the absence of probe sensitivity in low degree of monomer conversion. In order to check this possible behavior, the examined probes were warm up in THF in the presence of benzoyl peroxide. The changes in their, both, absorption and emission spectra were recorded for comparison. Figure 10 shows observed changes recorded during the heating at 55°C of **OS** probe solution in the presence of free radical source.

It should be pointed out that, the heating of probe in the absence of benzyl peroxide do not cause any changes in the absorption and fluorescence spectra. Inspection of the spectra shown in Fig. 10, reveals that when free radicals are formed, one observes substantial consumption of the probe (the absorption and emission intentensity decrease) that is

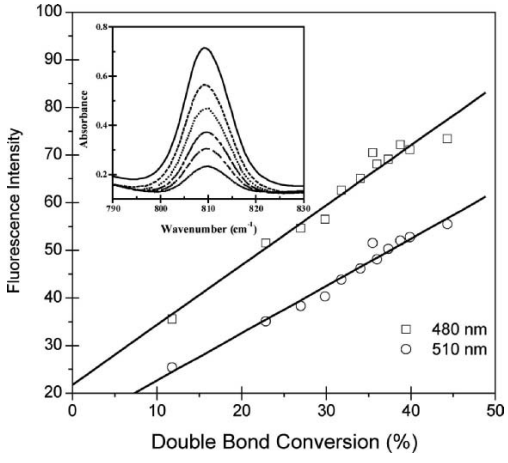


Fig. 9 Fluorescence intensity (**OS** probe, recorded at $\lambda = 480$ and 510 nm) versus degree of double bond conversion during photoinitiated polymerization of TMPTA. Inset: Changes of the absorption of –C=C– stretching frequency for TMPTA recorded at 810 cm^{-1}

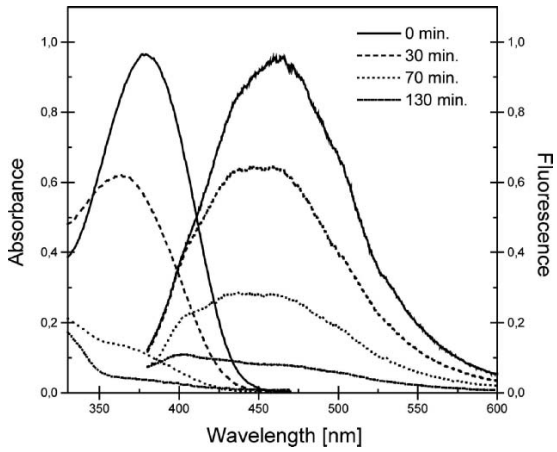


Fig. 10 Changes of the absorption and the fluorescence spectra observed during the heating (55°C) of **OS** probe in THF in the presence of benzyl peroxide. Fluorescence and absorption spectra measured after: (1) 30 min, (2) 70 min, (3) 100 min and (4) 130 min of heating

present in the system. This, in turn, may cause a progressive decrease of the probing sensitivity.

This problem can be avoid when the probe sensitivity is determined as the relationship between the ratio of emission intensities at two selected wavelengths (located at two sides of the emission maximum) and degree of vinyl monomer double bond conversion (Fig. 11).

Conclusions

In the context of the potential and practical applications of the styryl-like compounds, we have synthesized three dyes: 2-(*p-N*,*N*-dimethylaminostyryl)benzoxazole (**OS**), 2-(*p-N*,*N*-dimethylaminostyryl)benzothiazole (**SS**) and 2-(*p-N*,*N*-dimethylaminostyryl)-napthothiazole (**PS**). These compounds show unique solvatochromic behavior. The

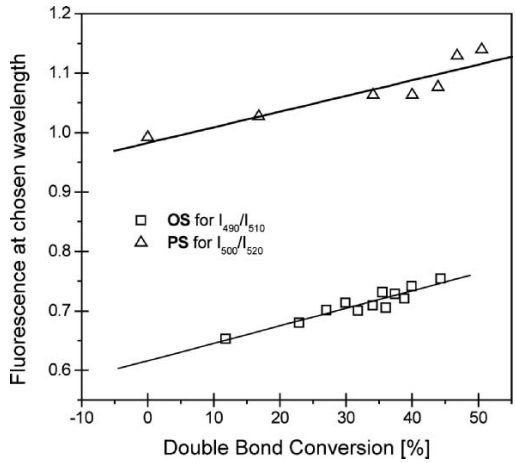


Fig. 11 Ratio of emission intensity at two selected wavelengths for **OS** and **PS** probes versus degree of double bond conversion during photoinitiated polymerization of TMPTA

significant red-shift of fluorescence maxima, as the solvent polarity is increasing, demonstrate the formation of an intramolecular charge transfer state.

Studied compounds can be used as spectroscopic probes monitoring the degree of cure of their environment. The study on the changes in the fluorescence intensity and spectroscopic shift of studied compounds were carried out during thermally or photochemically initiated polymerization. The examined probes are different in the behavior when they were used for the probing of polymerization of monofunctional monomer (methyl methacrylate (MMA)) and multifunctional monomer (2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA)). For monofunctionalized monomer, a rapid increase in fluorescence intensity is observed when the phase of the polymerizing system changes in the area close to gel point. This area is reached when the degree of methyl methacrylate polymerization is as high as 70–80% [32, 33]. Below this degree the polymer-monomer solution interacts with small probe molecule as typical nonviscous solvent [5, 34, 35]. On the other hand, the gel point for multifunctional monomers is reached below 5% of double bond conversion [36, 37]. Above this degree of double bond conversion, the probe molecule is enveloped by network chain that reduces the efficiency of nonradiative deactivation of the emitting state and causes an increase in fluorescence intensity. The specific differences in behavior of the probes observed during polymerization of mono- and multifunctional monomers originate from different properties of linear polymer solution and solution of network forming system.

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